

Solvent effect on vibrational frequencies: cryosolution experiments and density functional calculations

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Abstract

FTIR spectra of C₂H₆, COF₂ and CH₃F in the vapour phase and in solutions in liquefied argon, krypton and xenon were investigated. Vapour–solvent frequency shifts (SFS) were determined for all IR-active fundamentals of the studied compounds. In parallel, the SFS values were calculated using the Self-Consistent Isodensity Polarizable Continuum Model (SCIPCM) at the B3LYP/6-311++G(d,p) level. Comparison of the experimental and the calculated data shows reasonable agreement only for three most intense IR bands under investigation, i.e., the C=O and the CF₂ asymmetric stretching modes of COF₂, and the C–F stretching mode of CH₃F. For the other bands of COF₂, CH₃F and for all the bands of C₂H₆ the results of SCIPCM calculations underestimate the observed SFS significantly. It is concluded that at least for the modes with relatively small $(\partial\mu/\partial Q)_0$ values, the electrostatic interactions give a minor contribution to SFS. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solvent induced vibrational frequency shifts (SFS) have attracted interest for many years, since they provide important information on chemical bonding and solute–solvent interactions. It is known that intramolecular frequency shifts are determined by the normal coordinate dependant parts of the attractive and repulsive interactions between solute and solvent molecules [1]. The attractive interactions are usually subdivided into electrostatic, dispersive and specific ones. Separation of the different contributions to observed FS usually represents a complicated problem.

Several theoretical approaches were derived for

predicting SFS. An extensively developed approach is based on applying the hard fluid model [2–4]. In this, the contribution of repulsive interactions to SFS is calculated from the solvation mean force exerted along the bond axis of the hard sphere diatomic solute. The contribution of attractive interactions is usually obtained by fitting the experimental SFS at ambient conditions, and assuming that this contribution is linearly related to the density of the fluid [2–4]. According to the hard fluid model, the blue shift, produced by the repulsive interactions, has a magnitude comparable to that of the red shift which is caused by the attractive interactions. For the majority of liquids under normal conditions of temperature and pressure the attractive interactions slightly dominate, which leads to net red SFS [2–4]. Unfortunately, application of the hard fluid model to a particular system requires the magnitudes of the “hard-core

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